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# PHOTOEMISSION AND SECONDARY ION MASS SPECTROMETRY STUDY OF URANIUM PASSIVATION BY C[+] IMPLANTATION

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## 1 INTRODUCTION

Preventing the corrosion and oxidation of uranium is important to the continued development of advanced nuclear fuel technologies. Knowledge of the surface reactions of uranium metal with various environmental and atmospheric agents, and the subsequent degradation processes, are vitally important in 21st century nuclear technology. A review of the oxidation of actinide elements and their use in catalysis[1] summarizes the present understanding of the kinetics and mechanisms of the reaction in dry and humid air.

Researchers have recently used $N_2^+$ and $C^+$ ion implantation to modify the near surface region chemistry and structure of U to affect the nucleation and growth kinetics of corrosion and to passivate the surface.[2-4] These researchers used Auger electron spectroscopy (AES) in conjunction with sputter depth profiling to show that the implanted surfaces had compositional gradients containing nitrides and carbides. In addition to chemical modification, ion implantation can create special reactive surface species that include defect structures that affect the initial absorption and dissociation of molecules on the surface, thus providing mechanical stability and protection against further air corrosion.

## 2 METHOD AND RESULTS

Oxidation of the polished U in laboratory air prior to introduction into the ion implanter vacuum chamber results in a ≤20 nm oxide that was sputtered during the ion irradiation.[5] The implantation was performed on the water-cooled, lightly oxidized U sample at $10^{-7}$ Torr, normal incidence using $CO_2$ gas as the source material in a hot filament ionizer. A magnet separated the carbon +1 ions and the beam was rastered onto the surface resulting in a pure and uniform C dose accurate to a few percent. The TRIM calculated sputtering rates of the surface oxygen and surface uranium by the implanting carbon ions are 44% and 23%, respectively. After a year in "standard" California environment (ambient temperature, 50% relative humidity), the appearance of the implanted area remained unchanged. X-ray photoelectron spectroscopy (XPS) core-level analysis and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were used to determine composition and bonding versus depth. The U sputter rate was estimated to be 2 nm/min. (SRIM-96).

Figure 1 presents the ToF-SIMS depth profile results from the 33keV, 4.3 x $10^{17}$ cm$^{-2}$ C$^+$ implantation. We observed a thin oxide layer as indicated by the high oxygen content present in the first 50 nm of the surface. Arkush, *et al*,[2] and Musket[4] observed a similar trend in the near surface elemental composition of C$^+$ implanted U with AES depth profiling. The carbon profile shows a well-defined implant layer between 25 – 225 nm with centroid at 125nm from the surface. This carbon profile is comparable to previous AES depth profile results[2,4] and in agreement with the implant depth (TRIM).
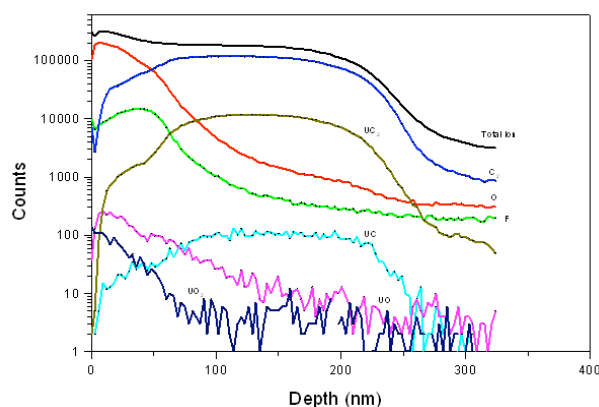


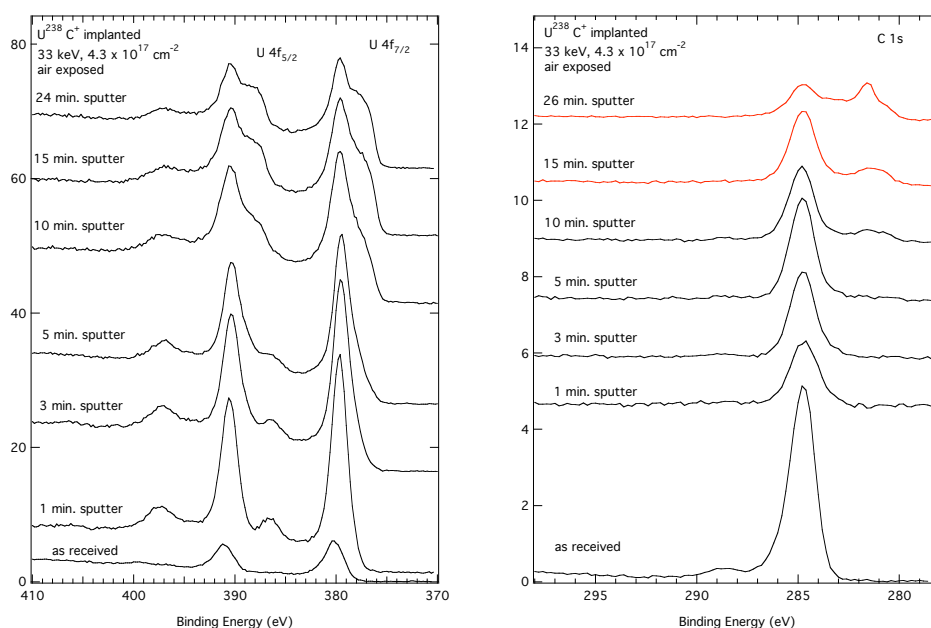**Figure 1**  *ToF-SIMS depth profile of the C$^+$ implanted region.*



**Figure 2**  *High-resolution U 4f$_{7/2,5/2}$ and C 1s core-level spectra versus sputtered depth for the C$^+$ implanted region.*

Figure 2(a) presents the high-resolution U 4f$_{7/2,5/2}$ core-level spectra for the C$^+$ implanted U surface as a function of sputter etch time. The U 4f$_{7/2,5/2}$ spin-orbit pair binding energies are in agreement with literature values for uranium in a U$^{4+}$ valence

state.[6-10] The initial spectra for the as received implanted surface do not exhibit the shake-up satellite feature due to excitation of an electron from the O $2p$–U bonding orbital to a partially occupied or unoccupied U $5f$ orbital, and indicative of stoichiometric $UO_2$.[6]

Following further sputter depth profiling of the $C^+$ implanted surface, the U $4f_{7/2}$ peaks show the presence of additional components, one at ~377 eV that represents the underlying metallic uranium,[7,10,11] and the second component at 378 eV that represents UC.[12,13] These facts compliment the ToF SIMS results showing the presence of a thin oxide layer on top of the U-carbide layer in the air exposed $C^+$ implanted area.

The high-resolution C $1s$ core-level spectra for the $C^+$ implanted U surface versus sputter etch time is presented in Figure 2(b). Sputter depth profiling of the $C^+$ implanted surface reveals a C $1s$ peak at 281.6 eV that is indicative of U-carbide.

The valence band region for the implanted U surface provided unique information about the electronic structure and the nature of chemical bonding in this implanted material. The results suggest that the UC has metallic character.

3 CONCLUSION

Core-level and valence band photoelectron spectroscopy in combination with time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiling of $C^+$ implanted U revealed a buried U-carbide layer with minimal residual oxidation at the carbide /U metal interface. The carbide layer strongly suppresses oxidation and has metallic character.

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